

Simple Model for Attraction between Like-Charged Polyions

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We present a simple model for the possible mechanism of appearance of attraction between like charged polyions inside a polyelectrolyte solution. The attraction is found to be short ranged, and exists only in presence of multivalent counterions. The attraction is produced by the correlations in the condensed layers of counterions surrounding each polyion, and appears only if the number of condensed counterions exceeds the threshold, $n > Z/2\alpha$, where α is the valence of counterions and Z is the polyion charge.

Polyelectrolyte solutions and charged colloidal suspensions present an outstanding challenge to modern statistical mechanics. One of the reasons for the great difficulty in achieving an understanding of these complex systems is due to the intricate role played by the counterions (microions) which counterbalance the much bigger charge of the polyions (macroions). Since the number density of counterions is so much greater than that of polyions it is the counterions that dominate the thermodynamic properties of polyelectrolyte solutions at low densities. The heterogeneity combined with the long-range Coulomb force makes polyelectrolytes almost impossible to study by the traditional methods of liquid state theory. It is, however, exactly this complexity that is responsible for the richness of the behaviors encountered in polyelectrolyte solutions and charged suspensions.

One of the most fascinating results of the subtle interplay of various interactions is the appearance of attraction between two like-charged macromolecules inside a solution or a suspension. This attraction is purely electrostatic and is not a result of some additional short-range van der Waals force. The attraction has been observed in simulations of strongly asymmetric electrolytes [1], as well as a number of experiments [2]. The exact mechanism responsible for this unusual phenomena is still not understood, although some theories attempting to explain its basis, have been recently advanced [3,4]. At this time, we believe, there exists a great need to explore

various simple models which might help shed additional light on the origin of this attraction.

Our discussion will be restricted to rodlike polyelectrolytes, a good example of which is an aqueous solution of DNA segments. Let us consider the simplest model of such a polyelectrolyte solution. The polyions shall be represented by rigid cylinders of net charge $-Zq$ distributed uniformly, with separation b , along the major axis of a macromolecule. The counterions shall be treated as small rigid spheres of charge αq located at the center. The counterions can be monovalent, divalent, or trivalent, for simplicity however, we shall restrict our solution to contain only one of the above types of counterions. An appropriate number of counterions is also present in the solution to keep an overall charge neutrality. The solvent shall be modeled by a uniform medium of a dielectric constant D . It has been argued by Manning that in the limit of very large Z and infinite dilution, a certain number of counterions will condense onto the polyions, thus renormalizing their effective charge. From a simple phenomenological argument Manning determined the number of condensed counterions to be $n_c = (1 - 1/\alpha\xi)Z/\alpha$ for $\xi > 1/\alpha$ and $n_c = 0$ for $\xi < 1/\alpha$, where $\xi = q^2/Dk_B T b$ [6]. Note that this result subtly depends on the order of the limits to be taken, first $Z \rightarrow \infty$ and then the infinite dilution. If the limits are interchanged no condensation will appear. Recently we have extended the Manning theory to finite concentrations and finite polyion sizes. In this case it is possible to show that

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the counterion association still persists, however, instead of a fixed number of condensed counterions associated with each polyion, we now find a distribution of clusters, each composed of **one** polyion and $1 \leq m \leq Z/\alpha$ associated counterions. The distribution of cluster sizes is well localized, and in the limit of large polyion charge and infinite dilution approaches a delta function centered on the value proposed by Manning, n_c [7].

Can the condensed layer of counterions be responsible for the observed attraction between two like charged polyions? To answer this question we propose the following simple model. Consider two parallel, rodlike polyions, with Z monomers, inside the polyelectrolyte solution. The separation between two macromolecules is d . If the attraction is produced by some sort of charge-correlation mechanism, we expect that it should be short-ranged. We shall, therefore, restrict our attention to distances such that $d < \xi_D$, where ξ_D is the Debye screening length. As was mentioned earlier, the strong electrostatic attraction between the polyions and the counterions favors the formation of clusters composed of one polyion and some number of associated counterions. For the purpose of this exposition, we shall neglect the polydispersity of cluster sizes and assume that both polyions have $n < Z/\alpha$ condensed counterions. It is important to remember that we are concerned with the interaction between the two polyions *inside* a polyelectrolyte solution. As was stressed before, an isolated polyion can confine counterions only if it is extremely long, while inside a solution the cluster formation can take place with the polyions of any size [7].

The associated counterions are free to move along the length of the polyions. We define the occupation variables σ_{ij} , with $i = 1, 2, \dots, Z$ and $j = 1, 2$, in such a way that $\sigma_{ij} = 1$ if a counterion is attached at i 'th monomer of the j 'th polyion and $\sigma_{ij} = 0$ otherwise. Since the number of condensed counterions is fixed by thermodynamics [7], the values of occupation variables obey the constraint $\sum_{i=1}^Z \sigma_{i1} = \sum_{i=1}^Z \sigma_{i2} = n$. We shall assume that the only effect of the counterion association is a local renormalization of the monomer charge. The Hamiltonian for this model takes a particularly simple form,

$$\mathcal{H} = \frac{1}{2D} \sum_{i,i'=1}^Z \sum_{j,j'=1}^2 \frac{q^2(1-\alpha\sigma_{ij})(1-\alpha\sigma_{i'j'})}{r(i,j;i',j')}, \quad (1)$$

where the sum is restricted to $(i,j) \neq (i',j')$, $r(i,j;i',j') = b\sqrt{|i-i'|^2 + (1-\delta_{jj'})x^2}$ is the distance between the monomers located at (i,j) and (i',j') , $\delta_{jj'}$ is the Kronecker delta, and $x = d/b$. Clearly, the above model is a great over-simplification of physical reality. The molecular nature of the solvent is not taken into account. The counterions are assumed to be confined to the surface of the polyions, while the polyions themselves are treated as completely rigid. Nevertheless, we believe that the simplicity of this phenomenological model, which allows us to perform exact analytic calculations, compen-

sates for its abstract nature. Evidently, if we can understand under what conditions the attraction can arise between two macromolecules in this idealization, in the future it might pave the way to a more complete, physically realistic model.

With this disclaimer in mind, we proceed to rewrite the Hamiltonian as $\beta\mathcal{H} = \xi H$, where $\beta = 1/k_B T$ and ξ is the Manning parameter defined earlier. The adimensional reduced Hamiltonian is

$$H = \frac{1}{2} \sum_{(i,j) \neq (i',j')} \frac{(1-\alpha\sigma_{ij})(1-\alpha\sigma_{i'j'})}{\sqrt{|i-i'|^2 + (1-\delta_{jj'})x^2}}. \quad (2)$$

Using a transformation of occupation variables defined by $\sigma'_{ij} = 1 - \sigma_{ij}$ it is easy to see that the Hamiltonian exhibits the following symmetry

$$H(Z, \alpha, \{\sigma\}) = (\alpha - 1)^2 H(Z, \alpha', \{\sigma'\}), \quad (3)$$

where $n' = Z - n$ and $\alpha' = 1 + 1/(\alpha - 1)$.

The partition function is

$$Q = \sum_{\{\sigma_{ij}\}}' \exp(-\beta\mathcal{H}) = \sum_{\{\sigma_{ij}\}}' \exp(-\xi H), \quad (4)$$

where the prime indicates that the occupation numbers are subjected to the constraints of the number of condensed counterion conservation. The symmetry relation (3) leads to invariance of the partition function, and any thermodynamic quantity derived from it, $Q(Z, n, \xi, \alpha) = Q(Z, Z-n, [\alpha-1]^2 \xi, 1+1/[\alpha-1])$. This property is quite useful when performing the calculations, since it reduces the ranges of parameters needed to study.

It is convenient to rewrite the partition function in terms of the variables $y_i = \exp(-\xi/i)$, $i = 1, 2, \dots, Z-1$, associated with the *intrapolyon* interactions and $z_i = \exp(-\xi/\sqrt{x^2 + i^2})$, $i = 0, 1, \dots, Z-1$, related to the *interpolyion* interactions. The partition function, for given values of Z and n , may be expressed as

$$Q = \sum_i^{N_c} \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{k=0}^{Z-1} z_k^{v_{ik}}, \quad (5)$$

where the sum runs over all the allowed configurations of counterions. The exponents u_{ij} and v_{ik} are quadratic polynomials in α with integer coefficients. For not too big values of Z , it is possible to generate the whole set of integers in the expression above, thus obtaining the partition function exactly. The force between the polyions may now be calculated through

$$F = \frac{1}{b\beta} \frac{\partial \ln Q}{\partial x}. \quad (6)$$

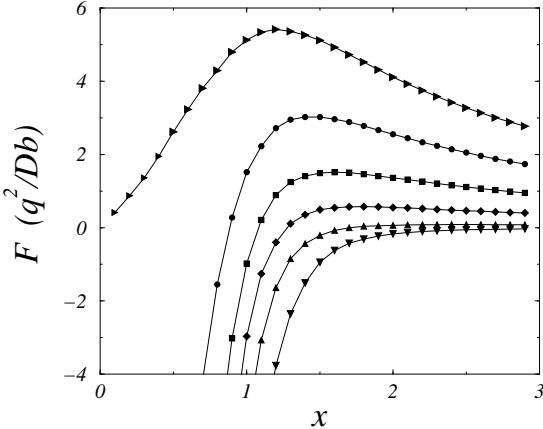


FIG. 1. Force versus distance between polyions for $Z = 20$, $\alpha = 2$, $\xi = 2.283$ (corresponding to polymethacrylate) and $n = 5, \dots, 10$ (from top to bottom) in the Monte Carlo simulation. The lines are only guides to the eye.

We find that at short distances and for $\alpha > 1$ the force between the polyions may become attractive (negative). The exact results are in full agreement with the Monte Carlo simulations which can also be extended to much larger values of Z , Fig. 1. For $\alpha = 1$ the force is always repulsive, which is in full agreement with the experimental evidence on absence of attraction if only monovalent counterions are present [2]. When the polyion charge is completely neutralized, $n = Z/\alpha$, the force becomes purely attractive, as can be seen in Figs. 1 and 2. Furthermore, the exact solution and the simulations indicate that a critical number of condensed counterions is necessary for attraction to appear, see Fig. 2.

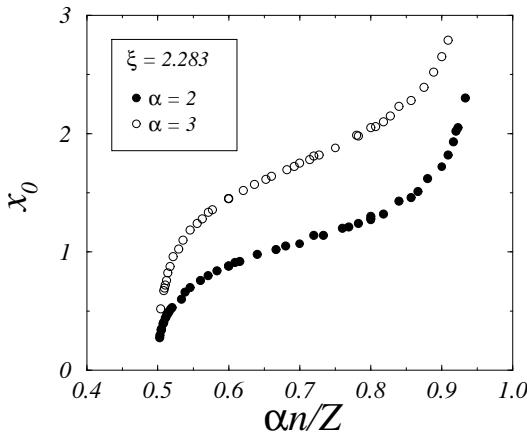


FIG. 2. Distance below which the polyion interaction becomes attractive versus the number of condensed counterion in the Monte Carlo simulation. Averages are over 100 sets and Z ranges from 20 to 200.

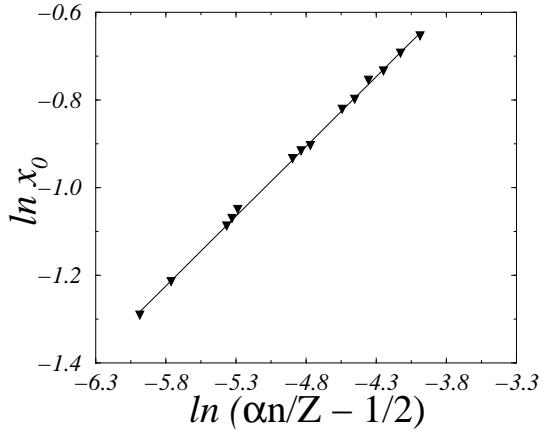


FIG. 3. Log-log plot near $n = Z/2\alpha$ for the $\alpha = 2$ data in fig. 2. The fit exponent is 0.32.

To simulate the model we use a standard Monte Carlo with particle-hole exchange, not restricted to nearest-neighbor pairs. This non local diffusion comes from the fact that the counterions may associate/dissociate at any point along the polyion. After thermalizing, both the energy and the force are measured, results being time and sample averaged. In Fig. 2 it is clear that the relevant parameter is the fraction of neutralized charge, $\alpha n/Z$, the curves for several values of Z (here from 20 to 200) collapsing on an universal function, deviations occurring only for very small Z .

As expected, the attractive interaction is short-ranged and at larger distances the force becomes repulsive. To further explore this point we consider the limit of small x . In this case the variable z_0 vanishes, while for finite ξ and Z all the other variables y_j and z_j remain positive definite. If we define $v = \min_i(v_{i,0})$, it is possible to rewrite the partition function as $Q = z_0^v W(1 + P)$, with

$$W = \sum_{i=1}^l \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{k=1}^{Z-1} z_k^{v_{ik}}, \quad (7)$$

and

$$P = \frac{1}{W} \left(\sum_{i=l+1}^{N_c} z_0^{v_{i,0}-v} \prod_{j=1}^{Z-1} y_j^{u_{ij}} \prod_{k=1}^{Z-1} z_k^{v_{ik}} \right), \quad (8)$$

where we suppose $v_{i,0} = v$ for the first l of the N_c configurations. As $x \rightarrow 0$, the function P vanishes, and we may use the approximation $Q \approx W z_0^v$. We then notice that v corresponds to the configurations which maximize the number of favorable horizontal interpolyion interactions,

$$v = Z - 2n\alpha \quad (9)$$

for $\alpha \geq 2$. Using the above approximation for the partition function we obtain

$$F \approx \frac{1}{b\beta} \left(\frac{1}{W} \frac{\partial W}{\partial x} + \frac{\xi v}{x^2} \right). \quad (10)$$

It is not difficult to see that the derivative of W vanishes as $x \rightarrow 0$, so that for small x we can Taylor expand the first term of Eq. 10. To leading order we find

$$f \equiv b\beta F \approx \frac{\xi v}{x^2} - hx, \quad (11)$$

where $h < 0$ (as v vanishes) is a function of the remaining parameters of the model. We notice that as $x \rightarrow 0$ the force vanishes if $v = 0$, is large attractive if v is negative, and is large repulsive if v is positive. In particular, in the limit $v \rightarrow 0^-$ the equilibrium distance is

$$x_0 \approx \left(\frac{\xi v}{h} \right)^{1/3} \sim \left(\frac{2n\alpha}{Z} - 1 \right)^{1/3}. \quad (12)$$

This scaling behavior is also observed in Monte Carlo simulations, Fig. 2 and 3.

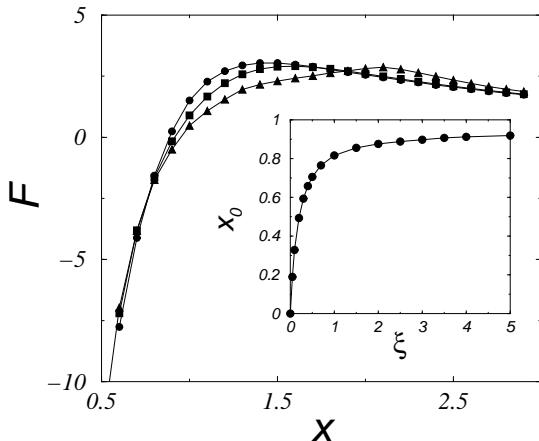


FIG. 4. Temperature dependence of the force between polyions for $Z = 20$, $n = 6$, $\alpha = 2$ and several values of ξ : 2.28 (circles), corresponding to polymethacrylate, 4.17 (squares), corresponding to DNA and 20 (triangles) for very low temperatures. The inset shows the distance x_0 at which the attraction first appears as a function of ξ . We see that for divalent counterions, $\xi = 1$ serves as a division point for the low and high temperatures regimes. Clearly for $\xi > 1$ the attraction is driven by the zero temperature mechanism!

We would like to stress that for a fixed number of condensed counterions the attraction is insensitive to the temperature (see figure 4). In fact the force between two lines at zero temperature ($\xi = \infty$) is almost exactly the same as at finite temperature, as long as the average electrostatic energy of interaction between two condensed counterions is greater than the thermal energy, $\alpha^2 q^2 / Dd > k_B T$, where d is the average separation between the condensed counterions. The mechanism for attraction between two like-charged rods is now clear [5]. At zero temperature the counterions on the two rods will take on staggered configuration, i.e. if the site of the first rod is occupied by a counterion the parallel site of the second rod will stay vacant. If the number of

condensed counterions is above the threshold $n = Z/2\alpha$ the favorable counterion-monomer interactions will outnumber the unfavorable monomer-monomer interactions, thus producing a net attraction at short distances. Using the threshold value of n we find that the attraction is dominated by the zero temperature correlations as long as $\xi > 2/\alpha$. On the other hand applying the Manning condensation criterion to the threshold number we see that the attraction is possible *only* if $\xi > 2/\alpha$. We thus come to an important conclusion: If the attraction exists it is produced by the zero temperature correlations.

In view of the current interest in the possible mechanisms responsible for the attraction between like charged objects it is worthwhile to make some further comments. A most common approach used to study this difficult problem relies on the field theoretic methodology similar to the one developed in Quantum Field Theory to study Casimir forces. The partition function is mapped onto an effective field theory which is then studied using a loop expansion. Due to the underlying difficulty of this process the expansion is usually terminated at the first loop level which is equivalent to the so called Gaussian approximation. The attraction, in this approach, arises as a result of the correlations in the Gaussian fluctuations [3]. Clearly from the above discussion this is not the mechanism responsible for the attraction between the two charged rods which was found by us. The problem with the field theoretic approaches used up to now is that the ground state energy was not properly treated.

Instead of allowing for a staggered configuration, which we found to be responsible for the attraction observed, the field theoretic approaches neglect the discrete nature of charges and uniformly smear the condensed counterions over the polyion. Clearly at zero temperature this can only result in a repulsion! The attraction, then, appears only as a finite temperature correction, produced by the correlations in the Gaussian fluctuations of the counterion charge densities on the two polyions, the effect which is much weaker than the one found by us to be responsible for the attraction. In view of our results we must conclude that the currently used field theoretic approaches [3] must be reexamined.

We have presented a simple model for the possible mechanism of appearance of attraction between the like charged polyions inside a polyelectrolyte solution. The attraction is found to be short ranged, and is possible only in a presence of multivalent counterions. The attraction is produced by the correlations in the condensed layers of counterions surrounding each polyion and extends uniformly from zero temperature. The attraction appears only if the number of condensed counterions exceeds the threshold, $n > Z/2\alpha$. Using the counterion condensation theory to estimate the number of associated counterions, we see that the attraction is possible only for polyelectrolytes with $\xi > 2/\alpha$. This is the fundamental result which has, evidently, gone unnoticed in the previous studies of this interesting phenomena.

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